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High Spatial Resolution Assessment of the Structure, Composition, and Electronic Properties of Nanowire Arrays

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ABSTRACT

We have employed transmission electron microscopy (TEM) and analytical electron microscopy to perform preliminary assessment of the structure, composition and electronic properties of nanowire arrays at high spatial resolution. The two systems studied were bismuth and bismuth telluride nanowire arrays in alumina (wire diameters ~40nm), both of which are promising for thermoelectric applications. Imaging coupled with diffraction in the TEM was employed to determine the grain size in electrodeposited Bi₂Te₃ nanowires. In addition, a composition gradient was identified along the wires in a short region near the electrode by energy-dispersive x-ray spectroscopy. Electron energy loss spectroscopy combined with energy-filtered imaging in the TEM revealed the excitation energy and spatial variation of plasmons in bismuth nanowire arrays.

INTRODUCTION

Nanowire arrays consisting of an ordered distribution of uniform diameter wires within a supporting matrix have attracted considerable recent interest.¹ These arrays can potentially be used to harness the properties of nanowires for robust applications in areas such as thermoelectrics, information storage, and photonics. Because transport in nanowires is confined to one dimension and the arrays have a large interfacial area, the array properties are particularly sensitive to even slight variations in structure and composition in the wires and at the wire-matrix interfaces. Therefore, to obtain an understanding of the relationship between the array characteristics and the array properties, it is necessary to assess the nanowires and wire-matrix interfaces at high spatial resolution.

In this work, we have focused on assessing the local characteristics in nanowire arrays of bismuth and bismuth telluride in alumina. These nanocomposite materials have potentially good thermoelectric properties.^{2,3} Thermoelectric materials are currently not in widespread use for cooling and power generation applications due to their relatively low efficiency. A promising approach to increase thermoelectric efficiency is through confinement of the charge carriers in low-dimensional structures, as demonstrated recently in quantum well systems,⁴ and this approach may be possible in two-dimensionally confined nanowires. The bismuth-alumina nanowire array system is also a good model system for understanding the relationship between

wire and interface characteristics and local electronic properties in arrays; this system is relatively simple and bismuth has interesting electronic properties due to its unique band structure. Bismuth telluride has good thermoelectric efficiency in bulk, and the bismuth telluride nanowire array system offers the possibility through manipulation of the wire composition to produce significant changes in the array properties.

In order to assess the local characteristics in these nanocomposite materials, characterization at high spatial resolution is required. Transmission electron microscopy allows for determination of the structure in the arrays with resolution of $\sim 2\text{\AA}$, and TEM coupled with analytical detection systems allows for determination of the composition and electronic properties in $\sim 1\text{nm}$ diameter regions of the specimen. Energy dispersive x-ray spectroscopy (EDS) in the TEM provides elemental composition information from the probed region. Electron energy loss spectroscopy (EELS) in the TEM in the low-energy loss region (0-40eV) is useful for studying valence excitations within the specimen, particularly collective electron excitations (plasmons). The goal of this work is to perform a preliminary assessment of the structure and composition in bismuth telluride nanowire arrays, as well as the electronic properties in bismuth nanowire arrays.

EXPERIMENTAL METHODS

The arrays were fabricated by deposition of the wire material into porous templates. Alumina templates were prepared by anodization of aluminum using a well-established process.⁵ Bismuth nanowire arrays were fabricated by pressure injection of molten bismuth into the pores of the template; this process has been described in detail elsewhere.⁶ Bismuth telluride nanowire arrays were prepared by electrodeposition into the templates. The procedure and more detailed characterization of the resulting arrays will be described in future work; here we give a brief overview of the process and a preliminary assessment of the wire structure. To deposit the wire material, an Ag film was sputter-deposited onto the top of the alumina template to serve as the electrode. The remaining aluminum was then chemically removed using a saturated HgCl_2 solution. The barrier layer created during anodization was removed from the pores by etching with KOH saturated in ethylene glycol. Bi_2Te_3 wires were formed by electrodeposition using a three-electrode set-up, with the Ag-backed porous alumina as the working electrode, Pt gauze as the counter electrode, and $\text{Hg}/\text{Hg}_2\text{SO}_4$ (in sat. K_2SO_4) as the reference electrode. Bismuth telluride was deposited in an ice bath from a solution of 0.0075M BiO^+ and 0.01M TeO_2^+ in 1M HNO_3 . The deposition potential was -0.60V relative to the reference electrode, which was chosen to be within the deposition range employed in previous Bi_2Te_3 film depositions.⁷

Samples were prepared for characterization in the TEM in two ways. To assess the structure and composition in individual nanowires, the wires were released from the alumina template by selective etching using a CrO_3 /phosphoric acid solution and then diluted through several replacements with water followed by ethanol. The nanowires were dispersed onto a holey carbon grid from the wire solution. To assess the electronic properties of the bismuth nanowire arrays, cross-sectional array specimens were prepared by dimpling followed by ion milling.

Assessment of the bismuth telluride nanowire structure, including imaging and diffraction, was performed using a JEOL 200CX TEM. The composition along individual nanowires was determined using a Philips CM200 TEM with a probe size of $\sim 1\text{nm}$ and an EmispecTM x-ray detection system for EDS. EELS studies were performed in the CM200 using a Gatan PEELS detection system.

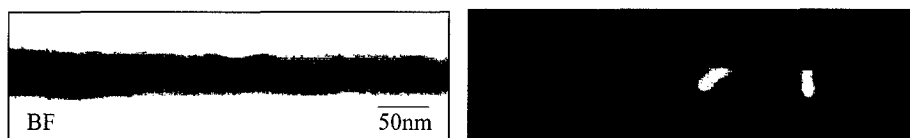


Figure 1. Bright-field (left) and dark field images of an individual Bi_2Te_3 nanowire.

RESULTS AND DISCUSSION

Bi_2Te_3 nanowire arrays

We have studied the structure and composition in the electrodeposited bismuth telluride nanowires. The average grain size in the wires was assessed using imaging combined with diffraction in the TEM. In figure 1, a bright-field image and corresponding dark-field image of an individual nanowire are shown. In the wires studied, the average grain size is smaller than the wire diameter, as illustrated in these images. The deposition parameters employed to produce these wires resulted in very fast pore filling. By varying the deposition conditions, including the deposition potential and temperature, it may be possible to vary the grain size. In addition, post-deposition annealing may be employed to increase the grain size. Such control is desirable because grain size has been shown to be an important factor governing the thermoelectric properties of bulk Bi_2Te_3 ^{8,9} and is expected to also play an important role in nanowire array properties.

In addition to wire structure, wire composition may also critically affect array properties. X-ray diffraction of the array structures indicates that the wires are Bi_2Te_3 , and EDS in the scanning electron microscope (SEM) shows a 2:3 Bi:Te ratio. In order to determine the composition of the individual wires, it is necessary to probe the wire composition at high spatial resolution. Therefore, EDS in the TEM has been employed to determine the composition in $\sim 1\text{nm}$ regions of the wire. Across the wire diameter and along most of the wire length, the composition is constant 40:60 Bi:Te within the error of the technique, which is approximately a few percent. However, near the electrode, there is a compositional gradient along the wire length, as indicated in Table 1. This gradient may result from the electrochemical deposition process. Further study is required to determine the origin of the gradient and to assess how well the composition can be controlled in this region. Such a gradient may have a significant effect on the array properties because transport in the wires is confined to the direction of the wire axis, and the properties of bulk Bi_2Te_3 are known to vary with even slight changes in stoichiometry.¹⁰

Probe position (relative to electrode)	Bi (%)	Te (%)
Near electrode	35.0	65.0
+ $\sim 6\mu\text{m}$	35.7	64.3
+ $\sim 1\mu\text{m}$	35.6	64.4
+ $\sim 1.3\mu\text{m}$	36.3	63.7
+ $\sim 1.6\mu\text{m}$	36.6	63.4
+ $\sim 2\mu\text{m}$	37.7	62.3

Table 1. Percentage of Bi and Te in $\sim 1\text{nm}$ regions of the wire relative to the electrode.

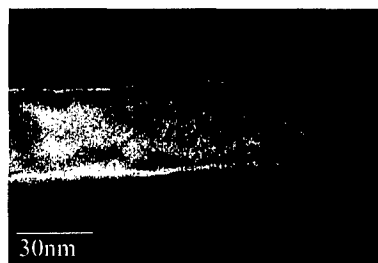
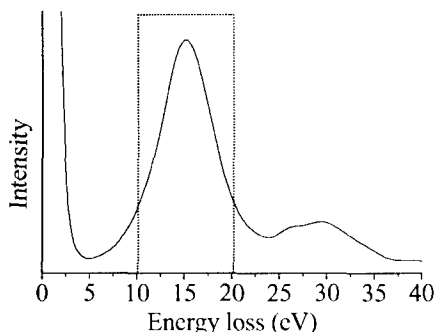


Figure 2. Energy-filtered image (above) created using electrons undergoing energy losses from ~ 10 – 20 eV, as indicated in the EEL spectra at right.



Bi nanowire arrays

In previous work, the characteristics of the wires and wire-matrix interfaces in pressure-injected bismuth nanowire arrays were described.¹¹ Here we report a preliminary assessment of the local electronic properties of the arrays as studied by EELS in the TEM. EEL spectra have been obtained with an ~ 1 nm probe size. The low-loss spectrum from the center of an individual bismuth nanowire is shown in Figure 2. The strong peak at ~ 15 eV is attributed to the bismuth volume plasmon. The two smaller peaks at higher energy loss (~ 26 and 29 eV) are due to the bismuth $O_{4,5}$ ionization edges.¹² The energy-filtered image in Figure 2 was created using a 10 eV energy filter to select the electrons that suffered an energy loss due to excitation of the 15 eV volume plasmon, as indicated by the highlighted region of the spectrum. Along the bismuth wire, variations in contrast are apparent. These variations result from diffraction contrast, which is preserved in the energy-filtered image due to the large signal-to-noise ratio present in low energy images.¹³ This image indicates that plasmon-loss images may provide additional useful information to help identify local strain fields within the wires. Identification of strain fields within nanoparticles is experimentally challenging using BF and DF imaging because such work involves extensive tilting of the specimen to align the particle in various zone axes, which is difficult to do with extremely small area particles.

In addition to studying the energy losses within the wires, EELS was also employed to assess the energy losses within the composite arrays. Spectra from the alumina template revealed an energy loss peak corresponding to the alumina bulk plasmon at ~ 26 eV, while spectra from the wires revealed the peaks described above. Using a ~ 1 nm probe at the wire-matrix interface, the spectrum shown in Figure 3 was obtained. Contributions from the bismuth and alumina bulk plasmons are apparent at ~ 15 eV and 26 eV, respectively. In addition, a lower energy peak (~ 5 eV) is also present. This energy loss is attributed to excitation of an interfacial plasmon.¹⁴

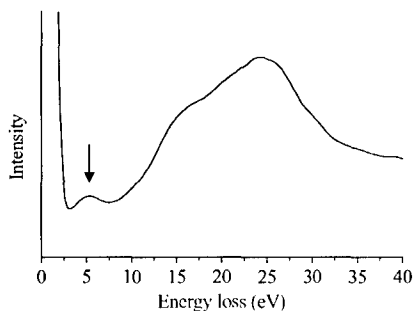


Figure 3. EEL spectrum obtained using an ~ 1 nm probe centered directly on the Bi- Al_2O_3 interface in an array.

CONCLUSIONS

TEM and analytical electron microscopy were employed to study the local characteristics of arrays of bismuth and bismuth telluride nanowires in alumina. Imaging in the TEM revealed that the average grain size in electrodeposited BiTe nanowires is smaller than the wire diameter ($\sim 40\text{nm}$). EDS of $\sim 1\text{nm}$ regions along the wire length indicated that the composition is constant except in a short region ($< 5\mu\text{m}$) near the electrode at the wire base. These results indicate that the local structure and composition in nanowire arrays may have a significant impact on the array properties.

Electron energy loss spectroscopy coupled with energy-filtered imaging was employed to assess the excitation energy and spatial variation of plasmons in individual bismuth nanowires as well as in a bismuth nanowire array. Energy filtered images of the bulk bismuth plasmon excitation in individual wires show a variation in intensity along the wire length due to diffraction contrast, which may provide useful information to identify regions of local strain within nanoparticles. In addition, a plasmon was identified at $\sim 5.5\text{eV}$ at the wire-matrix interface. These results demonstrate the usefulness of employing EELS in the TEM to assess the local electronic properties in nanocomposite materials.

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